

Module 4: TMR from isothermal DSC experiments

The natural logarithms of maximum heat release rates determined on each thermogram are plotted as a function of the inverse temperature in an Arrhenius diagram ($\ln q = f(1/T)$). This allows checking the Arrhenius law: the points are on a straight line.

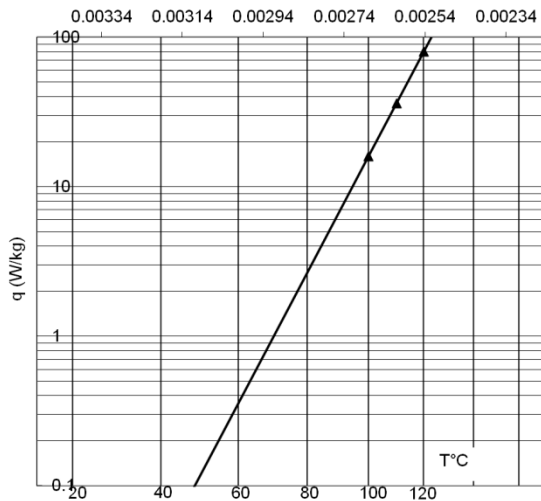


Figure: Arrhenius Diagram

From this diagram, the activation energy and the heat release rate for every temperature can be calculated. As an example, we take two points: 80 W/kg at 120°C and 16 W/kg at 100°C. With these values we calculate the activation energy as:

$$E = \frac{R \cdot \ln\left(\frac{q_2}{q_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{8.314 \cdot \ln(80/16)}{\frac{1}{373} - \frac{1}{393}} \approx 98150 \text{ J} \cdot \text{mol}^{-1}$$

Evaluation using Excel:

Temp C	T K	1/T	q W/kg	Ln q		
100	373.15	0.00268	16	2.77	Slope	-11818.5
110	383.15	0.00261	36	3.58	ln q0	34.43913
120	393.15	0.002544	80	4.38	Ea	98258.89 J/mol

Using this energy of activation and a heat capacity of $1.8 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, the TMR_{ad} can be estimated for a temperature of 80°C, where the heat release rate is 2.7 W/kg (extrapolation as zero order reaction):

$$\text{TMR}_{\text{ad}} = \frac{c'_p \cdot R \cdot T_0^2}{q'_0 \cdot E} = \frac{1800 \times 8.314 \times 353^2}{2.7 \times 98150} = 7037 \text{ s} \approx 2 \text{ hrs}$$

To obtain a TMR_{ad} longer than eight hours, the temperature must not exceed 65°C and 50°C for a TMR_{ad} longer than 24 hr.

Remark: the decomposition is autocatalytic (weak autocatalysis), since the maximum heat release rate is measured after an induction period. The time to maximum rate will be longer than the ones calculated here.